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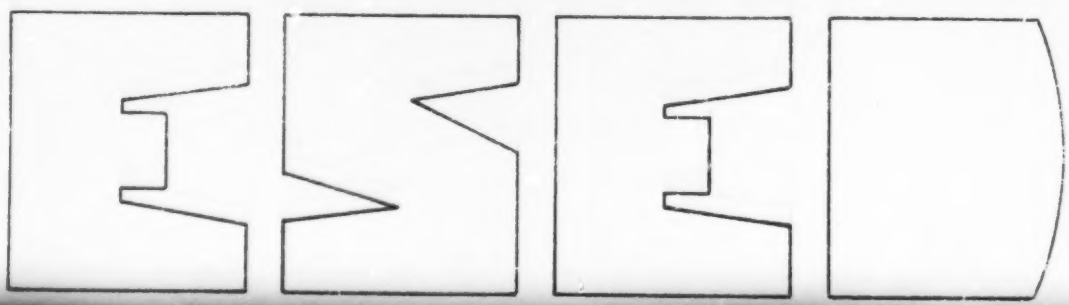

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16. ABSTRACT

This report discusses the development of Method 5B. Results from tests at fossil-fuel-fired boilers are summarized and compared.

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Development and Evaluation of Method 5B—Background Information for Proposed Reference Method

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
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Introduction

On June 11, 1979, the Environmental Protection Agency (EPA) promulgated standards of performance for new electric utility steam generating units. In the preamble to the regulation (44 FR 33580), EPA acknowledged that using Method 5 to sample for particulate matter in gas streams containing large amounts of sulfuric acid mist could lead to collection of condensed sulfuric acid mist as part of the particulate sample. Because particulate control devices, that were identified as best emission reduction systems, do not remove sulfuric acid mist, EPA concluded that the particulate matter sample should not include the condensed acid mist and agreed to develop a test procedure that would allow the measurement of nonsulfuric acid particulate matter (NSAPM).

Two approaches can be used to measure NSAPM. One is to use a sampling procedure that collects particulate but does not collect sulfuric acid, and the other is to use the existing sampling procedure (Method 5) and then remove any condensed sulfuric acid from the sample.

Conceptually, the first approach seems easier, but it presents some difficult problems in execution. The physical state of sulfuric acid in the stack depends on three variables, the temperature of the gas, the concentration of water vapor, and the concentration of sulfur trioxide (SO_3). As an example, at 155°C and 10 percent water vapor, a gas stream can contain about 82 ppm of uncondensed SO_3, but at 150°C and 10 percent water vapor, a gas stream can contain only about 52 ppm. This makes it obvious that one needs to control the temperature of the sampling system very precisely and evenly to prevent the collection of condensed sulfuric acid, but the sampling equipment used with Method 5 does not lend itself

readily to this kind of precise temperature control. Higher sampling temperatures could be used, but construction materials become a problem. Removing condensed sulfuric acid after sampling has two major advantages: (1) It allows the tester greater flexibility in the choice of sampling equipment and conditions, and (2) it confines operations requiring very precise control to the laboratory. For these reasons, the second approach, that of removing any condensed sulfuric acid after the sample is collected, was chosen as the more promising one.

Of the possible procedures for removing condensed sulfuric acid, the two most commonly used are: (1) heating the samples in an oven to evaporate the sulfuric acid before weighing, and (2) weighing the samples to constant weight, then chemically measuring the condensed sulfuric acid and subtracting its weight. These two techniques were compared using particulate samples collected at a coal-fired power plant burning a very high sulfur coal and equipped with a wet scrubber. For this set of samples, the two techniques gave comparable results for NSAPM.

Each technique has its own advantages and disadvantages. The heating technique is relatively quick and simple, but it is not specific for condensed sulfuric acid since any substance that has a similar boiling point would also be evaporated. The analysis/subtraction technique is more specific since there are very few interferences with the chemical measurement, but it is more time consuming and requires a very accurate weighing of the sample while it still contains sulfuric acid. This can be difficult because sulfuric acid is very hygroscopic, and the samples may

not reach constant weight. Because the heating technique seemed to have fewer problems, it was the technique chosen for initial development.

Method Development

A working method tentatively entitled Method 5B was drafted. The method allowed the tester the option of collecting samples at any temperature up to 260°C, but specified that the samples be returned to the laboratory and heated in a laboratory oven at 160°C for 3 hours before desiccating and weighing.

To determine the effect of sample collection temperature, a series of comparative tests were conducted at three different sites. Two of the test sites were coal-fired boilers, and the other was an oil-fired boiler. The sulfur content of the fuel varied according to site. A series of paired samples were collected at each site using a dual train system. The filter and sample probe of one train was maintained at 121° $\pm$ 25°C as specified in Method 5, while the filter and probe of the other train was maintained at 160° $\pm$ 25°C. The samples from all sites were first desiccated at room temperature and then weighed. Following this initial weighing, samples from some sites were extracted with isopropyl alcohol (IPA) to remove the sulfuric acid. The IPA extract was then analyzed for sulfuric acid by barium-thorin titration and the resultant weight of sulfuric acid was subtracted from the initial sample weights. Samples from other sites were heated to 160°C for 3 hours, desiccated, and weighed. All samples from a particular site were treated in the same manner.

The results from these tests are summarized in Tables 1 - 3. As expected, the initial sample weights of the samples filtered at 121°C were consistently higher than those filtered at 160°C. This can easily be seen from the tables. However, after both pairs of samples were treated to remove the condensed sulfuric acid, this relationship did not really change. Although the differences between Method 5 and 5B samples became smaller, the samples collected by Method 5 were still consistently higher than those collected by Method 5B. This can also be seen clearly from the tables. Although the reason for this difference could not be determined, it was apparently related to the relative amounts of condensed sulfuric acid collected with the sample.

The Environmental Monitoring and Systems Laboratory of EPA conducted similar tests concurrent with the testing described above. Their report also concluded that "sampling below the acid dew point and failure to keep the particulate material dry during sampling cause a positive bias in the sample results - a bias that is not removed by washing with IPA or by heating to 316°C." While the source of this positive bias is unknown, it is clear that samples should not be collected at temperatures below the acid dew point. Therefore, the working draft of Method 5B was revised to require that samples be collected at temperatures of 160° $\pm$ 25°C. However, some questions remained as to the most suitable temperature for conditioning the filters in the laboratory prior to weighing.

Table 1. COAL-FIRED BOILER NUMBER 1

RATIO OF CONCENTRATION TO REFERENCE CONDITION

(Method 5B - Following IPA Extraction)

Sample method / Analysis condition	5	5B
Ambient	1.54	1.03
IPA extraction	1.15	1.00

Table 2. COAL-FIRED BOILER NUMBER 2

RATIO OF CONCENTRATION TO REFERENCE CONDITION

(Method 5B - Heated to 160°C)

Sample method / Analysis condition	5	5B
Ambient	2.58	1.07
Oven heat - 160°C	1.60	1.00

Table 3. OIL-FIRED BOILER

RATIO OF CONCENTRATION TO REFERENCE CONDITION

(Method 5B - Heated to 160°C)

Sample method / Analysis condition	5	5B
Ambient	6.73	3.80
Oven heat - 160°C	2.00	1.00

Using the revised draft of Method 5B, EPA began a second test program to evaluate the consistency of the method and to determine the effects of different conditioning temperatures on the measured NSAPM. Tests were conducted at two different sources. The first was a coal-fired boiler equipped with an electrostatic precipitator and a flue gas desulfurization unit, and the second was an oil-fired unit equipped with a mechanical dust collector. Both units were burning fuels with relatively high sulfur contents, ranging from 2.4 to 3.5 percent sulfur.

Samples were collected with a sampling system, called a quad train, which allows the tester to collect four simultaneous samples divided into two pairs, each pair of which is collected under the same conditions. The advantage of this system is that a large number of paired samples can be collected in a relatively brief period of time. This minimizes the effect of temporal variations in source emissions making comparison between sampling methods easier. A more complete explanation of this sampling system and it's operation can be found in the emission test reports.

The detailed sampling and analytical matrices for the coal-fired boiler are shown in Tables 4 and 5, and for the oil-fired boiler in Tables 6 and 7. All the samples were collected with the filter and probe operated at 160°F except for those samples where the probe was heated to 204°F. There were two basic patterns of analysis. Most samples were desiccated at ambient temperature and weighed, and then conditioned in a laboratory oven at temperatures varying from 160°C to 316°C for periods of 6 to 24 hours before being desiccated and reweighed. The remaining samples were

Table 4. SAMPLE MATRIX FOR COAL-FIRED BOILER

Run no.	Sample train no.	Sample method[a]		
		M5B 160°C (320°F)	M5B-P400 160°-204°C (320°-400°F)	M5W 160°C (320°F)
1	1A	X		
	1B	X		
	1C			X
	1D			X
2	2A		X	
	2B		X	
	2C	X		
	2D	X		
3	3A			X
	3B			X
	3C	X		
	3D	X		
4	4A	X		
	4B	X		
	4C		X	
	4D		X	
5	5A	X		
	5B	X		
	5C	X		
	5D	X		
6	6A	X		
	6B	X		
	6C			X
	6D			X
7	7A		X	
	7B		X	
	7C	X		
	7D	X		
8	8A			X
	8B			X
	8C	X		
	8D	X		
9	9A	X		
	9B	X		
	9C		X	
	9D		X	
10	10A	X		
	10B	X		
	10C	X		
	10D	X		

[a] M5B - Probe and filter heated to 160°C (320°F).
M5B-P400 - Probe heated to 204°C; filter heated to 160°C.
M5W - Probe and filter heated to 160°C; water rinse of nozzle, probe, and front filter holder glassware.

Table 5. ANALYTICAL MATRIX FOR COAL-FIRED BOILER

Run no.	Sample train no.	Sample method	Thermogravimetric conditioning[a]			Water soluble sulfate determination[b]
			Ambient 160° 232° 316°C	Ambient 232° 316°C	Ambient 316°C	
1	1A	M5B	X			X
	1B	M5B	X			X
	1C	M5BW				
	1D	M5BW				
2	2A	M5B-P400	X (24)			
	2B	M5B-P400	X			
	2C	M5B	X (24)			
	2D	M5B	X			
3	3A	M5BW				
	3B	M5BW				X
	3C	M5B				X
	3D	M5B			X	
					X (24)	
4	4A	M5B		X		
	4B	M5B			X	
	4C	M5B-P400		X		
	4D	M5B-P400			X	
5	5A	M5B	X			
	5B	M5B	X (24)			
	5C	M5B		X		
	5D	M5B		X (24)		
6	6A	M5B	X			
	6B	M5B	X			
	6C	M5BW				
	6D	M5BW				X
						X
7	7A	M5B-P400	X			
	7B	M5B-P400	X (24)			
	7C	M5B	X			
	7D	M5B	X (24)			
8	8A	M5BW				
	8B	M5BW				X
	8C	M5B	X (24)			X
	8D	M5B	X (24)			
9	9A	M5B			X (24)	
	9B	M5B		X (24)		
	9C	M5B-P400			X (24)	
	9D	M5B-P400		X (24)		
10	10A	M5B	X (24)			
	10B	M5B	X			
	10C	M5B		X (24)		
	10D	M5B		X		

[a] Thermogravimetric conditioning of probe rinse and filter fractions at indicated temperatures after initial desiccation and ambient weights were obtained. The designation (24) for selected samples indicates a heat period of 24 hours. All other samples were heat-conditioned for 6 hours.

[b] In this procedure, the mass of total water soluble sulfates in the sample was determined and subtracted from the total sample mass.

NOTE: All back halves represent a modified Method 8, with analysis for sulfates as sulfuric acid and sulfur dioxide.

Table 6. SAMPLE MATRIX FOR OIL-FIRED BOILER

Run no.	Sample train no.	Sample method[a]		
		M5B 160°C (320°F)	M5B-P400 160°-204°C (320°-400°F)	M5W 160°C (320°F)
1	1A			X
	1B			X
	1C	X		
	1D	X		
2	2A	X		
	2B	X		
	2C			X
	2D			X
3	3A	X		
	3B	X		
	3C		X	
	3D		X	
4	4A		X	
	4B		X	
	4C	X		
	4D	X		
5	5A	X		
	5B	X		
	5C	X		
	5D	X		
6	6A	X		
	6B	X		
	6C	X		
	6D	X		
7	7A			X
	7B	X		
	7C			X
	7D	X		
8	8A	X		
	8B		X	
	8C	X		
	8D		X	
9	9A	X		
	9B	X		
	9C	X		
	9D	X		
10	10A	X		
	10B		X	
	10C	X		
	10D		X	

[a] M5B - Probe and filter heated to 160°C.
M5B-P400 - Probe heated to 204°C; filter heated to 160°C.
M5W - Probe and filter heated to 160°C; water rinse of nozzle, probe, and front filter holder glassware.

Table 7. ANALYTICAL MATRIX FOR OIL-FIRED BOILER

Run no.	Sample train no.	Sample method	Thermogravimetric conditioning[a]			Water soluble sulfate determination[b]
			Ambient 160° 232° 316°C	Ambient 232° 316°C	Ambient 316°C	
1	1A	M5BW				X
	1B	M5BW				X
	1C	M5B	X			
	1D	M5B	X			
2	2A	M5B	X (24)			
	2B	M5B	X (24)			
	2C	M5BW				X
	2D	M5BW				X
3	3A	M5B	X			
	3B	M5B	X			
	3C	M5B-P400	X			
	4D	M5B-P400	X			
4	4A	M5B-P400	X			
	4B	M5B-P400	x			
	4C	M5B	X			
	4D	M5B	X			
5	5A	M5B	X			
	5B	M5B	X			
	5C	M5B	X (24)			
	5D	M5B	X (24)			
6	6A	M5B		X (24)		
	6B	M5B		X (24)		
	6C	M5B		X		
	6D	M5B		X		
7	7A	M5BW				X
	7B	M5B		X		
	7C	M5BW				X
	7D	M5B		X		
8	8A	M5B	X (24)			
	8B	M5B-P400	X			
	8C	M5B	X (24)			
	8D	M5B-P400	X			
9	9A	M5B			X (24)	
	9B	M5B			X (24)	
	9C	M5B			X	
	9D	M5B			X	
10	10A	M5B		X		
	10B	M5B-P400		X		
	10C	M5B		X		
	10D	M5B-P400		X		

[a] Thermogravimetric conditioning of probe rinse and filter fractions at indicated temperatures after initial desiccation and ambient weights were obtained. The designation (24) for selected samples indicates a heat period of 24 hours. All other samples were heat-conditioned for 6 hours.

[b] In this procedure, the mass of total water-soluble sulfates in the sample was determined and subtracted from the total sample mass.

NOTE: All back halves represent a modified Method 8, with analysis for sulfates as sulfuric acid and sulfur dioxide.

treated with ammonium hydroxide to convert any sulfuric acid to ammonium sulfate before the total particulate matter was weighed. The water soluble sulfate content was then measured by a separate method and subtracted from the total particulate matter weight. This procedure, identified as Method 5W here, is a modification of a procedure used by the Texas Air Control Board. The full text of the procedure can be found in the emission test reports.

Discussion

The results from the coal-fired boiler test are summarized in Table 8, and the results from the oil-fired boiler test are summarized in Table 9. The average and 95 percent confidence interval for the average of these data are shown graphically in Figures 1 and 2.

There are some noticeable differences in the results from the two separate tests. Perhaps, the most striking is that the samples from the coal-fired boiler experienced the largest weight change going from ambient conditioning to conditioning at 160°C, while the samples from the oil-fired boiler showed the greatest change between conditioning at 225°C and 316°C.

As expected, the particulate weight measured by Method 5W was, in general, lower than that measured after heating, though those samples heated to 316°C showed relatively good agreement. This was expected since Method 5W measures all water soluble sulfates and not just sulfuric acid. It also indicated that ammonium sulfate which decomposes at 279°C was probably present in the samples.

Table 8. COMPARISON OF FILTERABLE PARTICULATE CONCENTRATION FROM A COAL-FIRED BOILER AFTER HEAT CONDITIONING AT INDICATED TEMPERATURES[a]

Run no.	Sample type	Ambient		160°C		232°C		316°C	
		Total weight, mg	Concentration, mg/dNm^3	Total weight, mg	Concentration, mg/dNm^3	Total weight, mg	Concentration, mg/dNm^3	Total weight, mg	Concentration, mg/dNm
1A	M5B	25.9	12.0	13.9	6.4	8.8	4.1	6.9	3.2
1B	M5B	79.7	37.6	16.0	7.5	10.3	4.9	8.9	4.2
2C[b]	M5B	56.6	28.5	18.2	9.2	19.4	9.8	14.6	7.4
2D	M5B	34.3	17.5	11.8	6.0	9.1	4.6	5.4	2.8
3C	M5B	58.8	18.9	-	-	-	-	13.1	4.2
3D	M5B	69.6	22.0	-	-	-	-	26.6	8.4
4A	M5B	26.7	7.8	-	-	12.1	3.5	11.0	3.2
4B	M5B	26.7	7.9	-	-	-	-	11.2	3.3
5A	M5B	47.6	14.2	21.1	6.3	17.1	5.1	14.7	4.4
5B[b]	M5B	46.2	13.9	16.3	4.9	17.9	5.4	13.9	4.2
5C	M5B	54.0	16.6	-	-	17.1	5.3	13.2	4.1
5D	M5B	48.2	14.8	-	-	16.4	5.0	13.2	4.1
6A	M5B	33.6	10.6	24.4	7.7	20.9	6.6	17.8	5.6
6B	M5B	33.8	10.7	19.5	6.1	15.5	4.9	11.6	3.7
7C	M5B	80.0	25.5	28.6	9.1	22.4	7.2	13.6	4.3
7D	M5B	86.3	26.5	31.3	9.6	30.4	9.3	26.5	8.1
8C[b]	M5B	92.3	29.5	19.0	6.1	19.7	6.3	15.5	5.0
8D	M5B	88.8	27.3	19.7	6.1	18.5	5.7	12.3	3.8
9A[b]	M5B	57.1	17.3	-	-	-	-	18.5	5.6
9B	M5B	58.2	17.8	-	-	25.4	7.8	20.5	6.3
10A[b]	M5B	45.0	13.5	25.5	7.7	24.8	7.5	21.2	6.4
10B	M5B	38.5	11.7	27.7	8.4	22.3	6.8	19.2	5.8
10C[b]	M5B	85.4	26.3	-	-	30.1	9.3	25.9	8.0
10D	M5B	77.3	23.1	-	-	29.4	8.8	22.6	6.7
	Average		18.8		7.2		6.4		5.1
			σ^c = 7.8		σ^c = 1.4		σ^c = 1.9		σ^c = 1.7
			N = 24		N = 14		N = 20		N = 25

Table 8. COMPARISON OF FILTERABLE PARTICULATE CONCENTRATION FROM A COAL-FIRED BOILER AFTER HEAT CONDITIONING AT INDICATED TEMPERATURES[a] (Continued)

Run no.	Sample type	Ambient		160°C		232°C		316°C	
		Total weight, mg	Concentration, mg/dNm^3	Total weight, mg	Concentration, mg/dNm^3	Total weight mg	Concentration, mg/dNm^3	Total weight, mg	Concentration, mg/dNm^3
2A[b]	M5B-P400	29.1	14.2	17.2	8.4	17.3	8.4	14.1	6.9
2B	M5B-P400	26.2	13.0	12.6	6.3	8.7	4.3	7.0	3.5
4C	M5B-P400	40.8	12.0	-	-	18.6	5.5	15.8	4.7
4D	M5B-P400	27.2	7.9	-	-	-	-	12.4	3.6
7A	M5B-P400	46.4	14.1	26.5	8.0	22.0	6.7	15.7	4.8
7B	M5B-P400	38.0	11.6	20.5	6.3	19.3	5.9	17.1	5.2
9C[b]	M5B-P400	31.6	10.0	-	-	-	-	15.4	4.9
9D	M5B-P400	39.0	12.0	-	-	20.1	6.2	17.9	5.5
	Average		11.8		7.2		6.2		4.9
			σ^c = 2.1 N = 8		σ^c = 1.1 N = 4		σ^c = 1.4 N = 6		σ^c = 1.1 N = 8

a Includes both filter and probe rinse fractions.
b Heat conditioning intervals for these samples were 24 hours; all others were 6 hours.
c Standard deviation with N-1 weighting for sample data.
d Number of data points.

Table 9. COMPARISON OF FILTERABLE PARTICULATE CONCENTRATION FROM AN OIL-FIRED BOILER AFTER HEAT CONDITIONING AT INDICATED TEMPERATURES[a]

Run no.	Sample type	Ambient		160°C		232°C		316°C	
		Total weight, mg	Concentration, mg/dNm^3	Total weight, mg	Concentration, mg/dNm^3	Total weight, mg	Concentration, mg/dNm^3	Total weight, mg	Concentration, mg/dNm^3
1C	M5B	336.7	185.0	283.6	155.8	266.1	146.2	194.8	107.0
1D	M5B	309.3	168.9	265.6	145.1	251.0	137.0	226.1	123.5
2A[b]	M5B	389.7	196.5	337.9	170.4	326.6	164.7	222.2	112.0
2B[b]	M5B	378.0	190.5	327.7	165.2	304.2	153.3	175.9	88.7
3A	M5B	356.9	186.8	311.1	162.8	298.2	156.0	251.1	131.4
3B	M5B	376.6	199.2	332.4	175.8	317.1	167.7	241.7	127.8
4C	M5B	348.6	201.8	319.8	185.2	310.6	179.8	241.1	139.6
4D	M5B	346.0	196.5	317.5	180.3	306.2	173.9	234.6	133.2
5A	M5B	235.5	165.0	201.2	141.0	185.4	129.9	152.6	106.9
5B	M5B	230.9	163.5	196.0	138.8	182.8	129.5	120.0	85.0
5C[b]	M5B	219.2	167.2	186.1	142.0	178.5	136.2	103.7	79.1
5D[b]	M5B	217.9	163.7	183.5	137.9	173.7	130.5	113.3	85.1

Table 9. COMPARISON OF FILTERABLE PARTICULATE CONCENTRATION FROM AN OIL-FIRED BOILER AFTER HEAT CONDITIONING AT INDICATED TEMPERATURES[a] (Continued)

Run no.	Sample type	Ambient		160°C		232°C		316°C	
		Total weight, mg	Concentration, mg/dNm^3	Total weight, mg	Concentration, mg/dNm^3	Total weight, mg	Concentration, mg/dNm^3	Total weight, mg	Concentration, mg/dNm^3
6A[b]	M5B	229.3	161.1	-	-	182.8	128.5	127.5	89.6
6B[b]	M5B	216.8	155.3	-	-	168.3	120.6	101.2	72.5
6C	M5B	169.6	140.0	-	-	135.1	111.6	104.8	86.5
6D	M5B	186.1	150.3	-	-	145.1	117.2	113.0	91.3
7B	M5B	221.9	159.0	-	-	152.1	109.0	101.6	72.8
7D	M5B	215.5	157.3	-	-	153.0	111.7	93.5	68.2
8A[b]	M5B	156.8	181.1	105.6	121.9	100.2	115.7	51.5	59.5
8C	M5B	112.6	131.5	89.8	104.9	84.9	99.2	51.2	59.8
9A[b]	M5B	252.9	171.7	-	-	-	-	117.5	79.8
9B[b]	M5B	261.2	180.9	-	-	-	-	116.7	80.8
9C	M5B	204.7	151.8	-	-	-	-	122.1	90.6
9D	M5B	224.6	162.3	-	-	-	-	119.3	86.2
10A	M5B	260.6	171.8	-	-	203.1	133.9	157.8	104.0
10C	M5B	210.0	159.6	-	-	176.8	134.4	123.5	93.8
Average		169.9 σ^c = 18.3 N = 26		151.9 σ^c = 23.0 N = 14		135.7 σ^c = 22.3 N = 22		94.4 σ^c = 22.5 N = 26	

Table 9. COMPARISON OF FILTERABLE PARTICULATE CONCENTRATION FROM AN OIL-FIRED BOILER AFTER HEAT CONDITIONING AT INDICATED TEMPERATURES[a] (Continued)

Run no.	Sample type	Ambient		160°C		232°C		316°C	
		Total weight, mg	Concentration, mg/dNm^3	Total weight, mg	Concentration, mg/dNm^3	Total weight, mg	Concentration, mg/dNm^3	Total weight, mg	Concentration, mg/dNm^3
3C	M5B-P400	335.2	211.1	296.8	186.9	284.2	179.0	230.8	145.3
3D	M5B-P400	351.4	193.8	314.3	173.4	300.3	165.6	245.7	135.5
4A	M5B-P400	398.9	202.2	369.1	187.1	357.7	181.3	291.5	147.7
4B	M5B-P400	398.0	194.0	365.6	178.2	349.9	170.5	276.8	134.9
8B	M5B-P400	111.5	134.5	87.9	106.0	79.3	95.7	59.1	71.3
8D	M5B-P400	105.5	133.2	85.3	107.7	74.2	93.7	55.7	70.3
10B	M5B-P400	226.1	151.6	-	-	179.9	120.7	136.0	91.2
10D	M5B-P400	213.8	158.8	-	-	181.6	134.9	124.7	92.6
Average		172.4		156.5		142.7		111.1	
		σ^c = 31.4		σ^c = 38.8		σ^c = 36.4		σ^c = 33.1	
		N = 8		N = 6		N = 8		N = 8	

a Includes both filter and probe rinse fractions.
b Heat conditioning intervals for these samples were 24 hours, all others were 6 hours.
c Standard deviation with N-1 weighing for sample data.
d Number of data points.

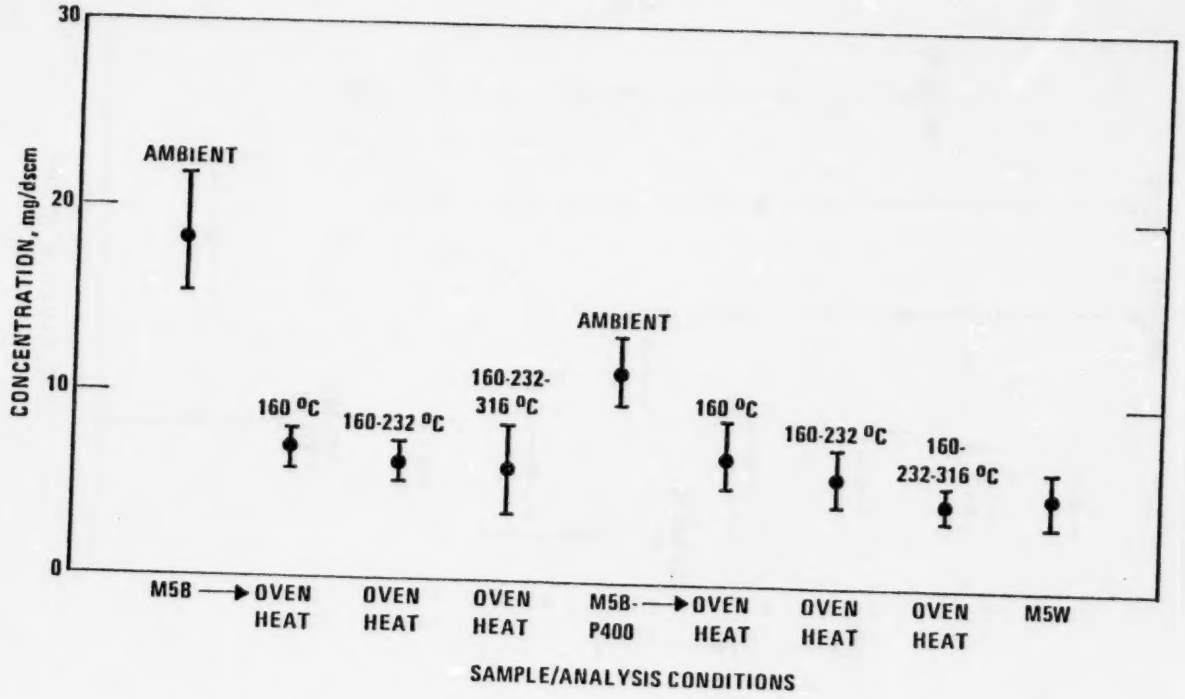

Figure 1. Coal-fired boiler.

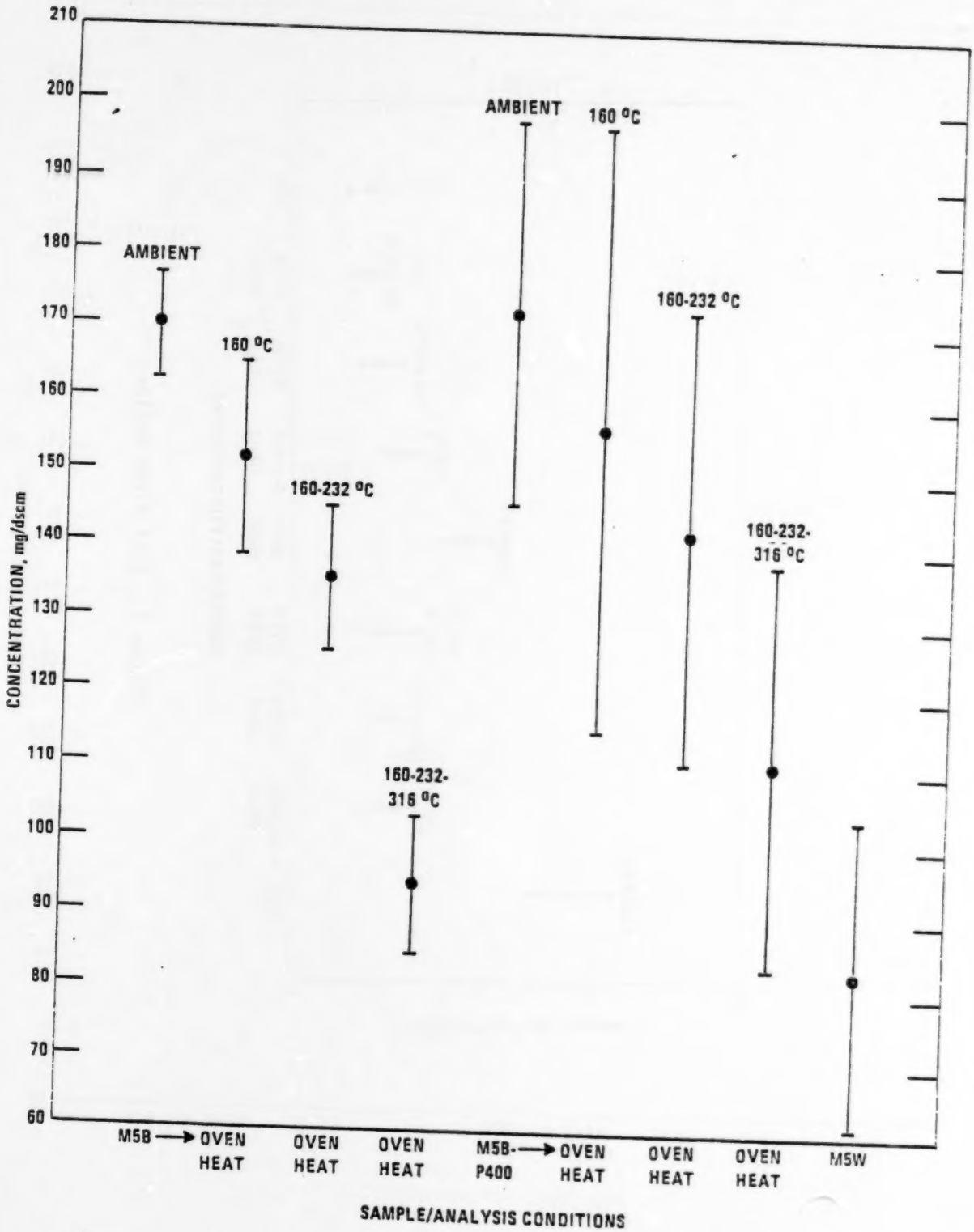

Figure 2. Oil-fired boiler.

One of the principal purposes of the testing program was to estimate the repeatability of Method 5B. As shown in Figures 1 and 2, the precision (which also includes temporal variations) of the method varies somewhat with the method of analysis. The poorest precision was usually produced by ambient conditioning followed by weighing while Method 5W usually showed the best precision. Some care must be exercised when analyzing the precision of the samples taken at the oil-fired boiler, because there were a number of process upsets during these tests which caused substantial variations in the emission rate from test to test. These variations between runs tend to obscure the variation between samples within a run. To eliminate this between-run variation, the standard deviation for the samples within a run were averaged over all runs for the different analytical techniques and plotted along with the 95 percent confidence interval of the average in Figures 3 and 4. These figures show that the samples from the oil-fired boiler follow a similar pattern to that of the coal-fired boiler.

When the results from the samples collected with the probe at 204°C are compared with those collected with the probe at 160°C, one can see that the samples collected with the higher temperature probe weigh less after ambient conditioning. This indicates that the higher probe temperature is successful in reducing the amount of condensed sulfuric acid collected. This is not unreasonable since it is more difficult to maintain an even temperature throughout the length of the probe, and the higher overall temperature is more likely to ensure that the gas stream does not contact any sections of the probe that are cooler than 160°C. However, after

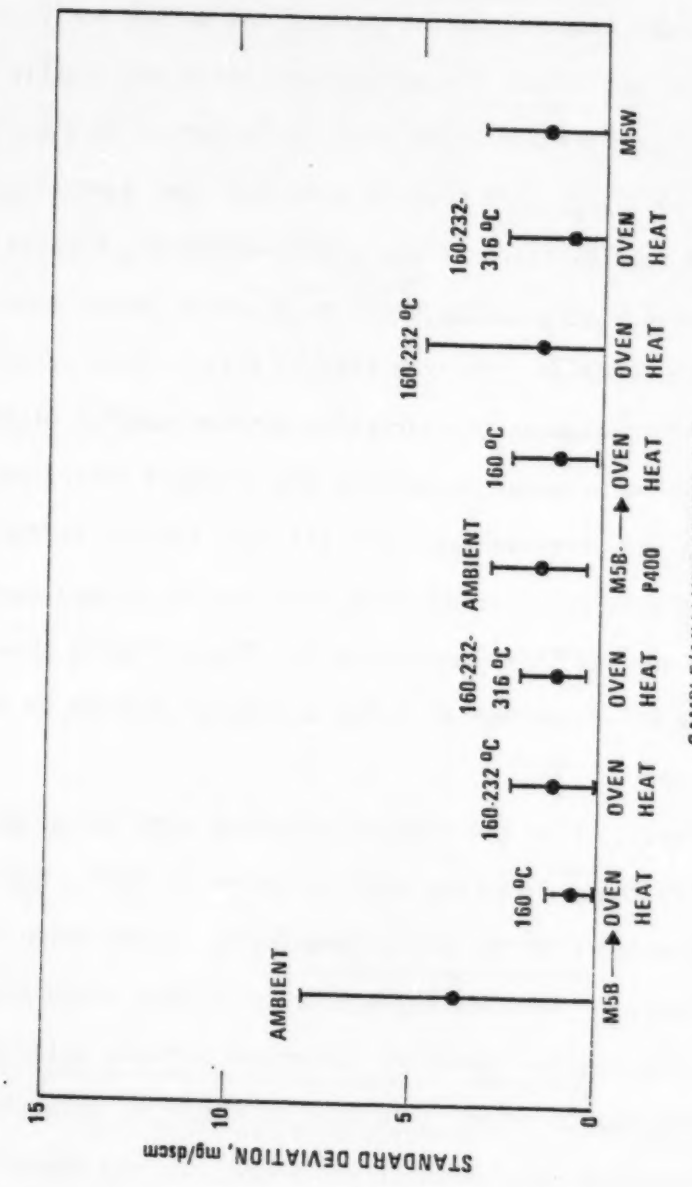

Figure 3. Coal-fired boiler.

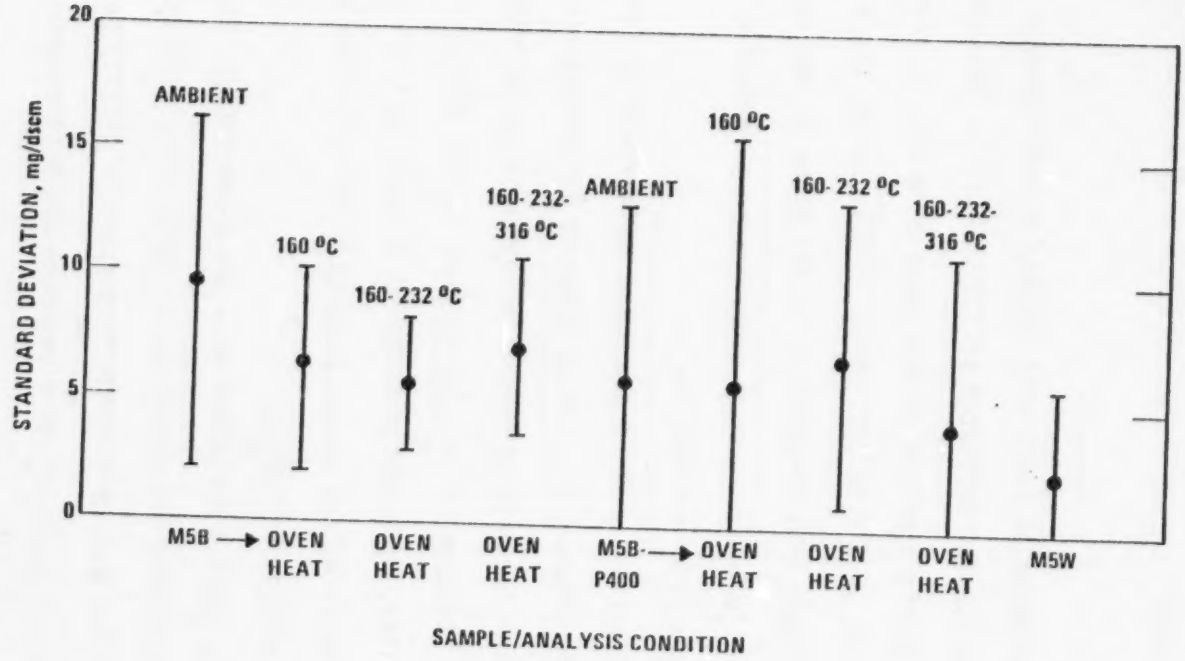

Figure 4. Oil-fired boiler.

conditioning the samples at temperatures of 160°C or higher, this difference in weight disappears. This is shown clearly in Tables 10 and 11. These tables are summaries of the data which have been normalized using Method 5B samples conditioned at 160°C as the reference.

Conclusions

Samples collected at 160°C will contain minimal amounts of sulfuric acid compared to samples collected at 120°C (250°F). While heating the probe to 204°C during sampling is even more effective in preventing condensed sulfuric acid from collecting on the sample, the extra effort required to maintain this temperature in the probe is not justified since any condensed sulfuric acid can be satisfactorily removed by heating the sample in an oven after collection.

The repeatability of the measurement is improved by heating the samples to 160°C after collection as compared to ambient conditioning, but there is little or no gain in precision upon heating to higher temperatures. Although, of all the methods tested, Method 5W showed the best repeatability, it cannot distinguish between sulfuric acid and other water soluble sulfates and is not a suitable technique for measuring NSAPM from electric utility boilers.

Collecting samples for NSAPM at a probe and filter temperature of 160°C and conditioning these samples at 160°C prior to weighing is the best technique for measuring NSAPM from electric utility boilers. The conditioning temperature of 160°C provides the best compromise between

Table 10. COAL-FIRED BOILER

RATIO OF CONCENTRATION TO REFERENCE CONDITION

(M5B heated to 160°C)

Condition / Analysis	Sample	M5B	M5B-P400	M5W
1. Ambient desiccation		2.61	1.64	--
2. Oven heat:				
Sequenced	160°C	1.00	1.00	--
	232°C	0.89	0.86	--
	315°C	0.71	0.68	--
3. Water extraction		--	--	0.71

Table 11. OIL-FIRED BOILER

RATIO OF CONCENTRATION TO REFERENCE CONDITION

(M5B heated to 160°C)

Condition / Analysis	Sample	M5B	M5B-P400	M5W
1. Ambient desiccation		1.12	1.13	--
2. Oven heat:				
Sequenced	160°C	1.00	1.03	--
	232°C	0.89	0.94	--
	315°C	0.62	0.73	--
3. Water extraction		--	--	0.55

a temperature high enough to evaporate any condensed sulfuric acid but not so high as to decompose or evaporate other materials which are intended to be counted as particulate matter.

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